

(12) **UK Patent Application** (19) **GB** (11)

2 161 647 A

(43) Application published 15 Jan 1986

(21) Application No 8417584

(22) Date of filing 10 Jul 1984

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(51) INT CL⁴
H01L 41/18 41/22

(52) Domestic classification
H1E 12 5 8 F G

(56) Documents cited
GB 1466704 GB 1090908

(58) Field of search
H1E

(54) **Pizeoelectric devices**

(57) A piezoelectric device comprises a thin layer 12 of piezoelectric ceramic material mounted upon a substrate 10, wherein: the layer of piezoelectric ceramic material is a composition of a "piezoelectric" ceramic in powder form distributed within a continuous phase of a glass-like binding agent, and is formed and thereafter electrically polarised *in situ*.

The layer of piezoelectric ceramic may be of laminated construction. The piezoelectric material may consist of a lead zirconate/titanate compound in a lead borosilicate binder. A liquid carrier is further included so as to produce a paste suitable for screen printing.

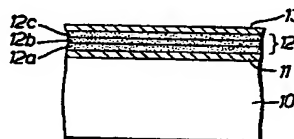


Fig.2.

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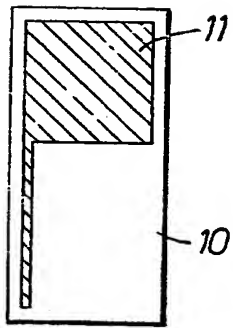


FIG. 1A.

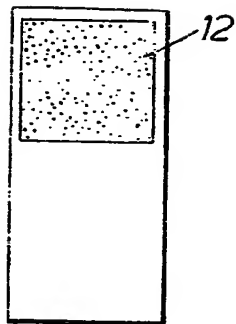


FIG. 1B.

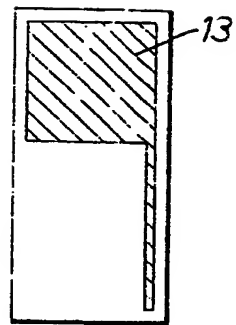


FIG. 1C.

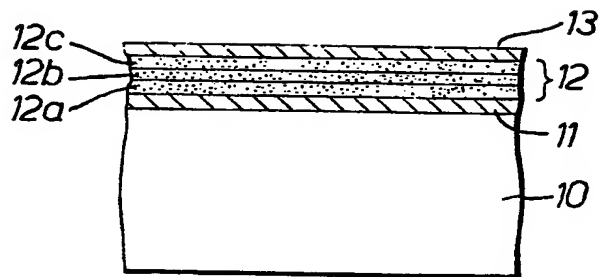


FIG. 2.

SPECIFICATION

Piezoelectric devices

5 This invention relates to piezoelectric devices. In particular, it concerns such devices wherein the piezoelectric element is formed using a method involving the screen printing (or like application) of a layer of a pastey composition, subsequently cured and polarised, upon a suitable substrate.

Technical Background

10 It is well known that a number of materials exhibit piezoelectricity—that is, they generate electricity under mechanical stress (and also physically deform under electrical stress). The phenomenon can be observed spontaneously in a crystalline substance such as quartz. It is a direct result of the anisotropy of the crystalline structure of the quartz (the non-symmetrical nature of the crystals, so that they look, and behave, differently depending on the angle of view relative to the crystal axis). Certain ceramic materials—such as lead zirconate titanate (PZT)—are molecularly, and even microscopically, anisotropic but nevertheless apparently isotropic in bulk because 25 their anisotropic characteristics are negated by the pseudo isotropy induced by the random order of the bulk material. They can, however, be made to exhibit piezoelectricity by introducing anisotropy into the bulk material, and what allows this to be done is the ferroelectric effect, which is analogous to the more widely known ferromagnetic effect. In order to introduce into such a medium the anisotropy needed for piezoelectricity to exist, it must undergo a strong electric field. In this field the single “microcrystals” preferentially align themselves in the direction of the electric field. This effect is called “polarisation”. Because of the ferroelectric effect, when the electric field is removed there will be quite a considerable remanent polarisation—that is, the microcrystals will still be generally aligned—and the anisotropy so 40 resulting causes the material to exhibit piezoelectricity.

There are available a number of piezoelectric ceramics that have considerably higher piezoelectric coefficients than do “natural” substances such as quartz. In theory, this makes them more suitable for use in piezoelectric transducers to be employed for the detection and generation of mechanical stresses and sound. However, in a number of applications it is necessary to attach piezoelectric transducers to a structure so that they may induce and/or detect the vibrations in that structure without significantly affecting the vibratory properties of that structure. With conventional slabs of piezoelectric ceramic this is often not possible, because the thinnest available transducers—which are very expensive—are 0.2 mm thick (200 μm ; transducers smaller than this would be very delicate and difficult to handle). Some applications require three or more of these transducers per device, each positioned very accurately; to do this using discrete slabs of piezoelectric ceramic is very 60 difficult and time consuming. Moreover, there are

very few materials which have a thermal expansion coefficient matched to that of any available piezoelectric ceramic, and as a result many devices are constructed using mismatched materials, leading to unwanted thermally-induced stresses.

We have now found that by using a composite piezoelectric material, conveniently a paste that is screen-printed into place, there can be made *in situ* very thin transducers having mechanical and piezoelectric properties similar to those of the pure piezoelectric ceramic. The transducers can be positioned very accurately both quickly and cheaply, and by varying the composition of the piezoelectric material so the thermal expansion coefficient can be varied, and thus easily matched to that of the substrate.

In one aspect, therefore, the invention provides a piezoelectric device in the form of a thin layer of piezoelectric ceramic material mounted upon a substrate therefor, wherein:

the layer of piezoelectric ceramic material is a composition of a “piezoelectric” ceramic in powder form distributed within a continuous phase of a glass-like binding agent, and is formed and thereafter electrically polarised *in situ* to produce the desired piezoelectric device.

In a second aspect the invention provides a method for making such a piezoelectric device. Thus, it provides a method of constructing a piezoelectric device comprising a thin layer of piezoelectric ceramic material mounted upon a substrate therefor, in which method:

- 95 a) there is formed upon the substrate a thin layer of a paste-like “piezoelectric” composition made from
 - (i) a “piezoelectric” ceramic in powder form,
 - (ii) a glass-like binding agent in powder form, and
 - (iii) a liquid carrier;
- 100 b) the substrate-borne layer is fired, by heating it to the softening point of the glass-like binding agent; and
- c) thereafter the fired layer is electrically polarised to produce the desired piezoelectric device.

The technology involved is similar to that used in the fabrication of Thick Film microcircuits, where resistors, capacitors and conductors are placed (usually by screen-printing) onto a substrate in the form of a paste, and a subsequent heat treatment removes some of the components of the paste and leaves a hard, glass-like layer having the desired electrical properties. The method of the invention involves making a similar paste which, heated in the same way, leaves a hard, glass-like layer that when polarised becomes piezoelectric. The paste consists of 115 finely powdered piezoelectric ceramic mixed with a glass-like powder binder and a liquid carrier.

Piezoelectric ceramics all have very similar properties, so the type used is not critical. The main factors affecting the choice are the specific piezoelectric properties of the ceramic and its maximum operating temperature. One suitable piezoelectric ceramic is VERNITRON PZT5A, which is believed to be a complex lead zirconate/titanate of the empirical formula $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ (where x is probably in the range 0.3 to 0.6). It

most likely contains a small amount of dopant ions such as Nb^{5+} , Ta^{5+} or La^{3+} . Other piezoelectric ceramics are of the same basic form but contain different amounts of dopant ions and have a different value of x . Examples of such other, important, piezoelectric ceramics are BaTiO_3 and PbNb_2O_6 .

The piezoelectric device of the invention comprises a thin layer of piezoelectric ceramic material mounted on a substrate. The term "thin" here means a few tens of micrometers thick—generally more than 10 but less than 100 μm . Moreover, while such a device could employ one only layer of piezoelectric ceramic, it is very possible, with such thin layers, that any one layer will have "pinholes" or other defects running through it, seriously reducing the desired piezoelectric properties of the device. It is preferred, therefore, that the "layer" be in the form of a laminated composite—a group of very thin layers (lamellae) one on top of the other, building up to the thickness finally required of the piezoelectric "layer". There may naturally be any number of such lamellae, though bearing in mind the minimum thickness of each (it is difficult to screen print, say, a paste layer less than 5 μm thick) and the maximum thickness of the composite (layers of much more than about 100 μm are getting somewhat too massive) there will preferably be no more than 10 lamellae. The actual number depends, of course, on the thickness of each and of the composite layer; in a preferred case (using 15 μm thick lamellae) there are only 3 or 4.

The layer of piezoelectric ceramic material is a composition of a "piezoelectric" ceramic in powder form and a binding agent (the expression "piezoelectric" is here used in quotes to indicate that the ceramic is at this point at best *capable* of being electrically polarised so that it exhibits piezoelectric properties).

The ideal grain size of the powder depends to some extent upon the method by which the layer is to be applied to the substrate, but will in any event be of the order of a few tens of micrometers and less. If placed in position by a screen printing process then naturally the grain size must be smaller than the holes in the screen. Equally, the grain size must be less than the thickness of the individual lamellae making up the layer, which commonly is of the order of 15 μm . In general, then, the grain size should be about 5 to 10 μm or less.

The glass-like binding agent powder is used to provide in the end product a continuous medium that both binds the piezoelectric powder together and bonds it all to the substrate surface. In the method of the invention the applied layer is heated to the softening point of the binding agent, at which temperature it flows slightly and forms a continuous layer around the "piezoelectric" ceramic grains and over the substrate. The binding agent is glass-like in that it has a non-crystalline nature, and softens and flows like glass at temperatures in the region of 450°C to 850°C depending on the type. Indeed, the agent may be a glass—generally, a composite of silicon oxide, sodium carbonate and calcium oxide, often with small amounts of other metallic oxides depending upon the exact properties required. A particular glass-like binding agent is lead borosilicate, which softens and flows in the region of 300°C to 500°C.

The ratio of binding agent to piezoelectric ceramic is not critical, but if there is too little agent the finished transducer will be powdery and not hard wearing, while if there is too much the piezoelectric properties of the layer will be too small to be of any use. As a rough guide the ratio by weight of piezoelectric ceramic powder to binding agent should be from 1:1 to 5:1.

The layer of piezoelectric ceramic material is formed and polarised *in situ*. One way of so forming it is, in accordance with the method of the invention, to apply to the substrate a layer of paste-like "piezoelectric" composition of the ceramic, the binding agent a liquid carrier, and thereafter to fire the paste layer. The prime purpose of the liquid carrier is to allow the composition to have the desired pasty nature, though a secondary purpose is to cause the layer to adhere to the substrate up to and during the firing process. The exact nature of the liquid carrier is not important, save that it enables production of the required pasty composition and be inert as regards the other components.

However, conveniently the liquid carrier is a mixture of at least two materials. The first is a volatile one which acts as a vehicle for the other components of the paste, and gives the paste the flow properties which make it suitable for printing (and after printing this material is preferably driven off by heating to a relatively low temperature, so "drying" the layer). The second material binds the applied layer together after the preliminary drying stage, and before the layer is heated to the softening point of the glass binding agent. In the firing, the second material is removed by "burning" at a temperature (of around 300°C, say) well below the softening point of the binding agent. The two materials are advantageously common organic "solvents" with boiling points in the appropriate ranges. Two typical materials are that mixture of $\text{C}_{10}\text{H}_{18}\text{O}$ terpene isomers known as terpineol (for the first—this is a solid at room temperature, but a liquid after slight warming) and ethyl cellulose (for the second—also a solid at room temperature, but when dissolved in the terpineol the resulting composition is liquid). Amounts of the order of 95 wt % terpineol and 5 wt % ethyl cellulose mixed together seem to make a satisfactory liquid carrier.

Although, of course, it is possible (when using the constructional method of the invention) to prepare the "piezoelectric" composition *ab initio*, starting with the individual raw ingredients, it is quite acceptable to blend the "piezoelectric" ceramic powder into a commercially-available paste of the desired nature, usually employing roughly 3 parts by weight of paste with 1 part by weight of ceramic powder. Standard "Thick Film" pastes (for example, those designated EMCA 2079-3 and EMCA 9121B, obtainable from Electro Materials Corp. of America) are available for printing insulating layers over conductors in Thick Film microcircuits. Commonly, these consist mainly of a glass binder (2079-3 is believed to be a lead borosilicate glass) and two organic materials as described above. By adding "piezoelectric" ceramic powder directly to one of these ready-mixed pastes there can be obtained a paste suitable for use in the format (by screen printing, say) of piezoelectric

transducers, though to obtain flow properties more appropriate for screen printing a few drops of liquid carrier (an organic solvent such as the proprietary EMCA EM FLOW 55; the exact composition of this is not known, but it is believed to contain terpenes) are added for every ounce ($\approx 30\text{g}$) of mixed paste. The exact nature of the materials in these two specific "Thick Film" pastes is not known, but they are slightly different, and give the paste slightly different properties. Thus, unlike EMCA 2079-3, in EMCA 9121B the glass binder devitrifies on firing—that is to say, when heated to its softening point it forms a polycrystalline structure, and does not soften when subsequently heated to its softening point. This is a useful property if it is desired to print further layers on top of the first layer. Secondly, 9121B contains small amounts of metal oxides which aid adhesion of the printed layer to substrates containing alumina.

Actual application of the piezoelectric ceramic layer to the substrate is, as will be apparent from the foregoing, most conveniently effected using printing, preferably a screen printing, process. The general concept of screen printing with a paste is well known, and needs no further comment here. Even so, it may be useful to outline it as a process in which a finely woven mesh (the screen) is first covered in the relevant areas with an impermeable layer which blocks the mesh to prevent passage of the paste therethrough, and then the paste is pressed (using the squeegee technique) through the unblocked areas of mesh onto whatever substrate is positioned beyond. Using very fine meshes (with as many as 325 holes per inch—128 holes per cm—say) there can be printed areas with an accuracy to as little as 0.1 mm.

Having formed the thin layer of piezoelectric material it is thereafter electrically polarised *in situ* so as to provide it with the required gross piezoelectric properties. This polarisation stage is well known *per se*, and no further comment need be made here. Nevertheless, very briefly it involves applying a strong d.c. electric field within the piezoelectric material at an elevated temperature. Under these conditions the piezoelectric microcrystals preferentially align themselves in a single direction. This is analogous to the process of orientating the domains in a ferromagnetic material to 'magnetise' it by applying a strong magnetic field at an elevated temperature. After a period sufficient to allow the alignment to finish, the material is cooled down while maintaining the field.

Applying this general technique to the piezoelectric composition used in the invention, there may be employed either a relatively high electric field at a low temperature or a relatively low electric field at a higher temperature. For example, satisfactory results can be obtained for a VERNITRON PZT5A composite with a field of 2000V/mm in the "piezoelectric" material itself at a temperature of 130°C or with the lower field of 200V/mm at the higher temperature of 360°C (which is the Curie point for PZT5A). The field/temperatures are conventionally applied for several minutes, and then, still maintaining the field, the piezoelectric material is allowed to cool slowly (at, say 10°C per minute) to around the 100°C mark, and then the field reduced to zero within a few minutes.

If the low temperature poling method is used it is

usually necessary to immerse the piezoelectric device in an insulating liquid such as silicone oil rather than performing the polarisation in air. This is because the field required is higher than that (about 1000V/mm) likely to cause dielectric breakdown of the air, so that a field great enough for the polarisation simply cannot be applied. In silicone oil, however, the field likely to cause dielectric breakdown is much greater, and polarisation can easily be performed.

The device of the invention comprises a thin layer of piezoelectric ceramic prepared *in situ* upon a substrate. This substrate may—provided it is physically and chemically stable to the ceramic layer and the methods employed in its formation—be of any convenient material. It may, for example, be a metal (such as INVAR R.T.M., and iron-nickel alloy containing 40-50 wt % nickel), a glass (such as one of those borosilicate-based glasses sold under the name PYREX R.T.M.) or a ceramic material (such as alumina), though preferably it is not a metal because of the poorer mechanical and thermal expansion matching, and the problems of ensuring the adhesion of the layer thereto.

One of the advantages of the device of the invention is that, because the piezoelectric layer is a composition whose ingredients may be varied both in nature and in quantity over quite a wide range, its physical characteristics—specifically its thermal and mechanical properties—can be "modified" to those of the substrate. For instance, it is generally desirable for the temperature coefficient of expansion of the substrate to match that of the piezoelectric layer. If this is not the case then thermally-induced stresses will occur at the interface between the two which will be weakened on repeated temperature cycling. By varying the content of the paste the net temperature coefficient of expansion of the piezoelectric layer can be made to match that of the substrate, thus avoiding the problem.

By way of example, it is noted that the thermal expansion coefficients of alumina and PZT5A are approximately 7 p.p.m./°C and 3 p.p.m./°C respectively. The net thermal expansion coefficient of a piezoelectric layer printed on alumina should preferably match that of the alumina, and this may be achieved by using an ink which contains equal volumes of PZT5A and a glass frit binder which has a thermal expansion coefficient of approximately 11 p.p.m./°C, such as that available from Schott Glass (Identity 8468) which is described as lead borate glass. On the other hand, to match to a lead borosilicate glass substrate the printed piezoelectric layer would preferably have a net expansion coefficient in the region of 3 to 4 p.p.m./°C, and this may be achieved by using a paste consisting of equal volumes of PZT5A and a glass frit binder with a similar thermal expansion coefficient, which may be a lead borosilicate glass similar to the substrate (but in the form of a frit or powder).

The inventive piezoelectric device has so far been described as though it comprised only a substrate bearing a thin layer of piezoelectric ceramic material. In practice, of course, to be a transducer of electrical into mechanical energy (or *vice versa*) the device requires means by which an electric field either may

be applied to the piezoelectric layer to cause it mechanically to deform or may be detected as it is generated within the layer when it is deformed. These means will preferably be two electrodes placed

5 "across" the layer — "across" meaning at either end (with the length or breadth of the layer between them) and/or on either face (with the thickness of the layer between them, so making an electrode/layer/electrode sandwich). This latter arrangement is preferred.

10 The material from which the electrodes are made can be any such material used or suggested for use in the Art (though, as explained below, certain restrictions may be placed upon this choice by any process employed to fashion the electrodes). They may, for example, be of noble metal, such as silver or gold, or of a cheaper good conductor such as copper or nickel. Silver electrodes presently seem preferable.

When electrodes are used as the means for applying/detecting electric fields, then they are most conveniently made as integral parts of the device. Indeed, just as the piezoelectric layer is formed *in situ*, so the electrodes may be formed *in situ*. Specifically, rather than use electrodes of, say, metal foil it is much preferred to prepare the electrodes in the same general way as the piezoelectric layer is conveniently prepared — namely, by constructing in the appropriate position a thin layer of a paste-like "electrode" composition that can be fired into a physically stable conductive form. The preparation of electrodes in this general manner is itself quite well known, and no more need be said about it here. Both gold and silver electrodes can relatively simply be formed in this manner, from a paste. Copper and nickel electrodes can also be prepared from a paste, but because of their chemical reactivity the paste needs to be fired in an inert atmosphere such as nitrogen, which may be rather inconvenient. A suitable electrode paste composition is the silver-containing "Thick Film" conductive ink available as EMCA 4175, and this may be applied by standard screen printing techniques. It should be noted, however, that the use of silver may cause problems if "dendritic" growth of a deposited silver layer is allowed to occur during the subsequent firing process. Such growth may short out the two electrodes.

As might be expected, it is very preferable to incorporate the construction of the electrodes in this manner into the method of constructing the piezoelectric device. Thus, for example, if the device is to be a transducer comprising a substrate, a first layer being an electrode, a second layer being the piezoelectric layer, and a final (top) layer being the second electrode, then the whole process involves first firing the electrode first layer on the substrate (applying and forming the conducting paste), then forming the piezoelectric layer on top of the electrode layer (applying and firing the piezoelectric paste), then forming the electrode top layer on the fired piezoelectric layer (applying and firing the conductive paste), and finally polarising the piezoelectric layer (conveniently using the two electrodes in this step).

As will be appreciated, by making use of the invention the active components of an entire transducer — the combination of electrodes and piezoelectric layer — may easily and accurately be formed *in*

situ, conveniently by a method involving a simple screen printing process, in any required position and shape.

The invention extends, of course, to a piezoelectric device, especially a transducer, whenever made in the manner described and claimed herein.

The following Example is now given, though only by way of illustration, to show details of the preparation of a piezoelectric transducer according to the invention. In this Example reference is made to the accompanying Drawings (which are *not* to scale), in which:

Figures 1 A, B and C show "plan" views of the various layers going to make up the device; and

Figure 2 shows a cross-section through the finished device.

Example: Preparation of a Piezoelectric Transducer
a) Preparation of a piezoelectric ceramic paste

A piezoelectric ceramic paste was prepared from the following ingredients:

EMCA 9121-B
(glassy binder) 3 parts by weight
VERNITRON PZT 5A
(20mm powder) 1 part by weight
EMCA EM FLOW 55 (thinner) a few drops

The PZT 5A is available as sheets. It was first crushed to a powder in a ceramic pestle and mortar, and then the resulting powder was passed through a fine mesh sieve to select only grains smaller than 20 μm . An initial paste was then made by mixing the EMCA 9121-B (which is a paste used for printing insulating layers over conductors on "Thick Film" microcircuits) and the finely powdered PZT 5A lead zirconate titanate in the ratio of 3 to 1 parts by weight. This formed a fairly stiff paste, not entirely suitable for screen printing, and a few drops of EMCA EM FLOW 55 thinning were added until the consistency of a thick creamy paste, more suitable for screen printing, was achieved.

b) Description of screen printing techniques

The printing was done using a standard technique, employing a polyester 325 mesh screen (a screen made up of fine polyester threads interwoven in two orthogonal directions such that there are 325 threads per inch). In this technique the substrate is placed a small distance beneath the screen, and the paste is placed on the screen. The action of applying pressure on the screen with a rubber squeegee and drawing the squeegee across the screen pushes the screen down onto the substrate and at the same time squeezes the paste through the holes in the mesh, leaving a thin layer of paste approximately 15 μm thick on the substrate.

To prevent paste being printed where it is not wanted the holes are first blocked using a standard photolithographic masking technique.

c) Formation of the device electrode and piezoelectric layers

The Reference Numerals included hereinafter relate to the accompanying Drawings.

The substrate employed was a flat sheet (10) of COORS ADS-96F alumina.

i) The lower electrode

A conductive layer (11) roughly 18 x 18 mm and about 15 μm thick was printed on the surface of the

substrate using the above-mentioned screen printing technique. The "ink" employed was EMCA 4175, which is a silver-containing "Thick Film" conductive ink. The shape and dimensions of this layer are shown

5 in Figure 1A.

This layer was dried in an oven for 10 minutes at 160°C to drive off the organic solvent. It was then heated, at a rate of about 20°C/minute, to 850°C to burn off the organic binder, and to soften and devitrify the
10 glass binder. It was held at this temperature for 10 minutes, and then cooled down to room temperature at a rate of approximately 20°C/minute.

ii) *The piezoelectric layer*

A composite layer (12) of piezoelectric ceramic made up of three individual lamellae (12, a, b and c) each roughly 19 x 19 mm and about 15 µm thick, was printed and processed, in the same way as the lower electrode layer, on top of the lower electrode. The pattern employed is shown in Figure 1B. Each lamella
20 was dried and fired before the next was printed thereon.

iii) *The upper electrode*

Finally, a second conductive 18 x 18 mm layer (13) of EMCA 4175 about 15 µm thick was printed on top of the piezoelectric layer (to the pattern shown in Figure 1C), and processed in the same way as described above. At this stage the device had the cross section shown in Figure 2.

d) *Polarisation of the piezoelectric layer*

The piezoelectric layer was then polarised using a standard low temperature technique. The piezoelectric device was immersed in a heated bath containing Dow Corning 200 silicone oil viscosity of 100cS). When the temperature of the bath had stabilised at around
30 130°C a potential difference was applied between the two electrodes of the piezoelectric device resulting in an electric field of approximately 20kV/mm. The electric field and the high temperature were maintained for about 10 minutes, after which time the electric field was slowly reduced to zero.
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e) *Testing of the device*

A convenient way of assessing the piezoelectric sensitivity of a device is to measure the piezoelectric voltage constant, which is defined as the electric field developed due to an applied mechanical stress divided by that stress. The prepared device had a piezoelectric voltage constant of the same order of magnitude as that of a slab of pure PZT5A.

CLAIMS

50 1. A piezoelectric device in the form of a thin layer of piezoelectric ceramic material mounted upon a substrate therefor, wherein:

the layer of piezoelectric ceramic material is a composition of a "piezoelectric" ceramic in powder
55 form distributed within a continuous phase of a glass-like binding agent, and is formed and thereafter electrically polarised *in situ* to produce the desired piezoelectric device.

2. A device as claimed in Claim 1, wherein the piezoelectric ceramic is VERNITRON PZT5A, which is believed to be a complex lead zirconate/titanate of the empirical formula $Pb(Zr_{1-x}Ti_x)O_3$ (where x is probably in the range 0.3 to 0.6).

3. A device as claimed in either of the preceding
65 claims, wherein the thin layer of piezoelectric ceramic

material is from 10 to 100 µm thick.

4. A device as claimed in any of the preceding claims, wherein the thin layer of piezoelectric ceramic is in the form of a laminated composite—a group of very thin layers (lamellae) one on top of the other, building up to the thickness finally required of the piezoelectric "layer".
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5. A device as claimed in Claim 4, wherein there are 3 or 4 15 µm thick lamellae.

6. A device as claimed in any of the preceding claims, wherein the particle size of the piezoelectric ceramic material is from 5 to 10 µm.

7. A device as claimed in any of the preceding claims, wherein the glass-like binding agent is lead borosilicate.
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8. A device as claimed in any of the preceding claims, wherein the ratio by weight of piezoelectric ceramic powder to binding agent is from 1:1 to 5:1.

9. A device as claimed in any of the preceding claims, wherein the substrate is a glass or a ceramic material.
85

10. A device as claimed in any of the preceding claims, wherein there are means by which an electric field either may be applied to the piezoelectric layer to cause it mechanically to deform or may be detected as it is generated within the layer when that is deformed, and these means are two electrodes placed across the piezoelectric layer.

11. A device as claimed in claim 10, wherein the electrodes are made of silver, gold, copper or nickel.

12. A piezoelectric device as claimed in any of the preceding claims and substantially as hereinbefore described.

13. A method of constructing a piezoelectric device as claimed in any of the preceding claims, in which method:
100

a) there is formed upon the substrate a thin layer of a paste-like "piezoelectric" composition made from

(i) a "piezoelectric" ceramic in powder form,
105 (ii) a glass-like binding agent in powder form, and (iii) a liquid carrier;

b) the substrate-borne layer is fired, by heating it to the softening point of the glass-like binding agent; and
c) thereafter the fired layer is electrically polarised
110 to produce the desired piezoelectric device.

14. A method as claimed in Claim 13, in which the liquid carrier is a mixture of at least two materials the first of which is a volatile one which acts as a vehicle for the other components of the paste, and gives the paste the flow properties which make it suitable for printing and the second of which binds the applied layer together after the preliminary drying stage, and before the layer is heated to the softening point of the glass binding agent.

15. A method as claimed in Claim 14, in which the first material is a mixture of $C_{10}H_{18}O$ terpene isomers known as terpineol, and the second is ethyl cellulose.

16. A method as claimed in Claim 15, in which there is 95 wt % terpineol and 5 wt % ethyl cellulose mixed together to make the liquid carrier.

17. A method as claimed in any of Claims 13 to 16, in which the actual application of the piezoelectric ceramic layer to the substrate is effected using a screen printing process.

18. A method as claimed in any of Claims 13 to 17,
130

in which the polarisation stage involves the application of a relatively high electric field at a low temperature.

19. A method as claimed in Claim 18, in which a field of 2000V/mm is applied at a temperature of 130°C.

20. A piezoelectric device, especially a transducer, whenever made in the manner claimed in any of Claims 13 to 19.

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